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Organic Emissions and Mercury Deposition: Connections to Agricultural and Biomass Burning and Climate Change

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The chemistry of the troposphere is complex and in many cases linked to emissions from man's activities and those emissions interacting with natural emissions (See Figure 1). Climate change is leading to a number of changes for the U.S. and the Southern United States that include increases in extreme events. These extreme

events include severe weather, flooding, droughts, as well as increases in heat advisories in summer months. While climate change is something we are now recognizing and will need to adapt to in the near future, changing some of our "habits" is likely one of the more difficult things we will face. Most of our attention

has been on the release of carbon dioxide from the use of fossil fuels, and associated emissions of air pollutants, particularly nitrogen oxides, that can lead to the formation of tropospheric ozone (also a greenhouse gas) and other oxidants such as peroxyacetyl nitrate (PAN). Though these are important, there are a number of significant impacts that can occur from agricultural and biomass burning (i.e. wildfires), and from volatile reactive organic emissions from vegetation that will increase as we warm the region and increase the length of the growing season (Gaffney and Marley, 2011). These organics rapidly oxidize in the atmosphere to form a wide variety of organic compounds many of them derived from isoprene and from monoterpenes such as alpha- and beta-pinene. These compounds are fairly water soluble and rapidly form atmospheric aerosols which are an important contributor to the haze seen over vegetated regions such as the Ozarks and the Great Smoky Mountains.

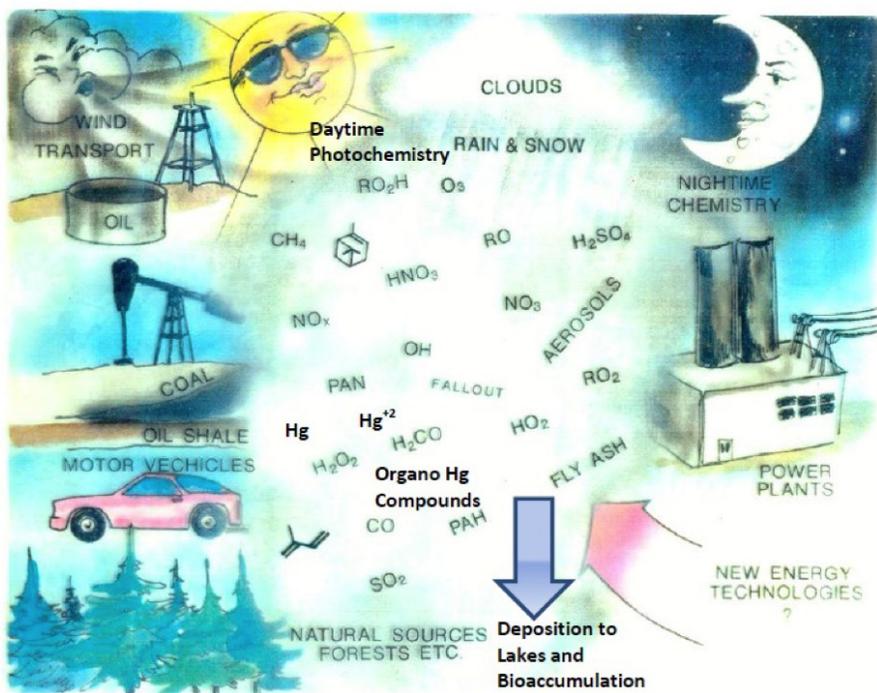


Figure 1. The complex environmental chemistry of Mercury in the atmosphere and its connection to agricultural and biomass burning. As noted, Hg can react with H₂O₂ to form Hg⁺². Mercury's complexation with Organo Hg compounds in clouds and wet aerosols and are water soluble lead to increasing deposition in lakes, and subsequent bioaccumulation in the fish through the food chain.

Ethene and formaldehyde (along with a myriad of organics and soot) are emitted at significant levels from the burning of biomass either from agricultural or wildfires, and are also emitted from burning ethanol fuels (Gaffney, et al. 2012). Ethene is a potent plant-growth hormone and its background levels are low (0.1 - 0.3 ppb) in the Southwestern and South Central U.S. (Gaffney, et al. 2012). Emissions from combustion of any type of biomass, particularly during uncontrolled burning such as agricultural burning or wildfires, are large. For example, approximately one gram per kilogram of biomass is emitted as ethene during combustion. Formaldehyde emissions are also very high from these sources with levels in the tenths of percent. (Gaffney, et al., 2012). If you have ever sat around a campfire and the wind blew the smoke in your face, or were downwind of your neighbors burning leaves then you recognize the burning and tearing from the smoke as one of the side effect of formaldehyde and other lachrymators such as acrolein that are emitted in high levels from these biomass burning activities.

While we have been putting controls on the emissions from fossil fuel fired power plants, motor vehicles, and other combustion sources, controls on agricultural burning practices are slow in coming. The impacts of these uncontrolled combustion sources are evidenced by data obtained here at the University of Arkansas at Little Rock (UALR) in Little Rock, AR. by examining atmospheric carbonaceous soot samples for their carbon-14 content. Carbon-14 content (modern carbon content) is a direct measure of the biomass contribution to the soot. Fossil fuel being millions of years old has essentially no ¹⁴C as its half-life is 5730 years. Biomass, however, is in equilibrium with atmospheric carbon dioxide that contains ¹⁴C which is cosmogenically produced in the lower stratosphere and upper troposphere. The ¹⁴CO₂ is then taken up into plants and distributed throughout the food chain. Soot ¹⁴C levels at UALR have been found to be typically

80% recent carbon. These same ¹⁴C contents have been found at similar or higher levels in many areas of the world pointing to the importance of the biomass burning as a major source of atmospheric soot worldwide (Gaffney and Marley, 2011). Indeed, even in Mexico City biomass contributions have been found to be a major source of atmospheric pollution, at times approaching 70% or more (Marley, et.al. 2009). This is a clear indicator that biomass burning of all types is contributing not only to atmospheric black carbon levels but also to the emissions of gases, such as ethene and formaldehyde, that accompany incomplete combustion.

These emissions of ethene and formaldehyde along with naturally increasing levels of isoprene (2-methyl-1,3-butadiene) initiate further chemical reactions in the atmosphere that lead to air pollution issues such as increased ozone levels under conditions where there is sufficient nitrogen oxides and also increased formation of peroxyacetyl nitrate (PAN). PAN is a very potent plant toxin and like ethene and ozone can cause plant damage and leaf senescence (Gaffney et al. 2012).

These atmospheric chemical reactions are driven by the conversion of nitric oxide (NO) to nitrogen dioxide by reactions with peroxy radicals, the simplest being hydroperoxyl radical or HO₂. As the emissions age and NO is removed as nitric acid or complexed as NO₂ with the peroxyacetyl radical (CH₃CO-OO) to form PAN (CH₃-CO-OO-NO₂), the reactions with HO₂ slow and the reaction of HO₂ with itself begins to form hydrogen peroxide by the following reaction:



A significant source of the HO₂ radical is formaldehyde, which photolyzes or reacts with OH radicals to form H atoms which add to oxygen. Ethene oxidation leads to formaldehyde as a secondary product as well and thus leads

to more hydrogen peroxide in our atmosphere. Hydrogen peroxide is very water soluble, being 7 orders of magnitude more soluble than oxygen or ozone, and is an important and often forgotten oxidant in cloud water and wet aerosols. It is one, if not the most important, route for oxidation of sulfur dioxide to sulfuric acid in the formation of “acid rain”. (Gaffney, et al. 1987).

Recently there has been a lot of news about increases of mercury in Arkansas Lakes giving rise to higher levels in larger fish species as the mercury is accumulated in the food chain. These increases are currently monitored by the Arkansas Department of Environmental Quality. There are a number of natural sources of mercury, including the mineral cinnabar (HgS). However, cinnabar has a very low water solubility, which reduces the environmental impacts of this mineral. The increases observed in the lake waters over the past decade are most likely due to atmospheric deposition. A recent in-depth review on the atmospheric chemistry of mercury and its links to waters and soils details the complex nature of the mercury cycle (Gaffney and Marley, 2014). One of the findings of this review was that the reaction of hydrogen peroxide with elemental mercury in cloud water and on wet aerosols and soil surfaces oxidizes it to mercury(II) followed by complexation with naturally occurring organics. This is likely leading to increases in both wet and dry deposition of mercury to soil and surface waters.

As noted earlier, hydrogen peroxide is formed in the atmosphere at low levels but is very water soluble and can concentrate in aqueous solution. It has been known for many years as an important reactant with sulfur dioxide to form sulfuric acid contributing to acid rain. This same reactant has been of concern in dentistry when hydrogen peroxide bleaching is used as a tooth whitening agent in patients with mercury amalgam dental fillings. Once the mercury is complexed with organics, which are primarily coming from the oxidation of terpenes emitted from the forests and plants as

well as from agricultural and biomass burning, it can enter the food chain and bioaccumulate in larger fish. This occurs in the oceans as well as in freshwater systems. As noted in a recent [brochure](#) funded by the Governor’s Mercury Task Force, and published by the Division of Health Education and Promotion and the Division of Epidemiology at the Arkansas Department of Health in cooperation with the Arkansas Game and Fish Commission, Arkansas Department of Environmental Quality, there are a number of precautions that should be taken that can allow us to learn to eat Arkansas fish safely.

It should be noted that there are natural mercury sources including volcanos that have always led to background levels of mercury in fish worldwide. The recent increases that have been seen worldwide are likely due to the release of the more volatile elemental Hg from anthropogenic sources. These include artisanal gold mining (primarily in Africa and South America), mining and smelting operations, and combustion of coal for energy in power plants. Thus, the major source of mercury to the atmosphere in Arkansas is from coal combustion. It is interesting to note that this same reaction of hydrogen peroxide (H₂O₂) with elemental Hg, which is likely adding to Hg deposition, has been successfully used to trap Hg emissions from coal fired power plants where it can be recycled or converted back to cinnabar. This has been accomplished in Germany and Sweden using the commercially available [MercOx process](#). This same process is being considered for use in soil remediation where higher levels of mercury have been found. What is important to realize is that the chemistry of mercury is complex and is always in equilibrium with many species in the atmosphere-biosphere-geosphere system, and that developing a better fundamental understanding of its chemistry leads to better ways to control its levels in our environment and our foods, and ultimately leads to a healthier planet. It is also important to note that a significant amount of its chemistry is tied to hydrogen peroxide, which is tied to

organic oxidation reactions via formaldehyde production. The formaldehyde is tied to both biomass burning emissions and also to natural vegetation emissions of isoprene and other terpenes, which are increasing as the temperature increases.

So how does this connect to climate change? With increasing temperatures and longer growing seasons in many areas, the potential for increasing wildfires is one of the main predictions coming out of the climate change reports. Increasing populations increase the demand for food and energy. With a push for more biomass fuels, such as ethanol the demand for the agricultural community to expand ethanol production will increase. That demand will lead to more agricultural burning, unless we come up with alternatives to that practice. Note that ethanol combustion also produces ethene, acetaldehyde, methane, and formaldehyde from incomplete combustion processes that occur in mobile vehicles and this will also have adverse effects on air quality (Tanner, et. al, 1987; Gaffney and Marley, 2009, Ginnebaugh and Jacobson, 2012).

Some alternatives to agricultural burning are collection of the biomass debris for use as an alternative fuel to coal in power plants. In a stationary contained power plant, the emissions can be controlled and energy obtained from the unwanted biomass debris. This would lead to employment opportunities in the collection of the material as well as in the production of biomass energy. This also would drastically reduce the release of harmful emissions into the atmosphere from continued uncontrolled burning (agricultural, trash, and leaf-burning activities, etc.), which will have a multitude of adverse effects on air and water quality as noted in the examples above.

How do we figure out if we were actually making a difference? Well, one important action to answer that question is to collect baseline data on a number of important chemicals in the

environment on a continuous basis at many sites all over the country and the world. The atmospheric observatory and measurements of the late Dr. David Keeling are well known for their importance in documenting carbon dioxide increases in the Northern Hemisphere. What we will need now and in the future is measurements on regional scales to evaluate the current levels of compounds like ethene and formaldehyde which may have a significant role in damaging crops and ecosystems in the future as climate change driven extremes increase.

Background Spectrum – FTIR – 0.5 cm^{-1}

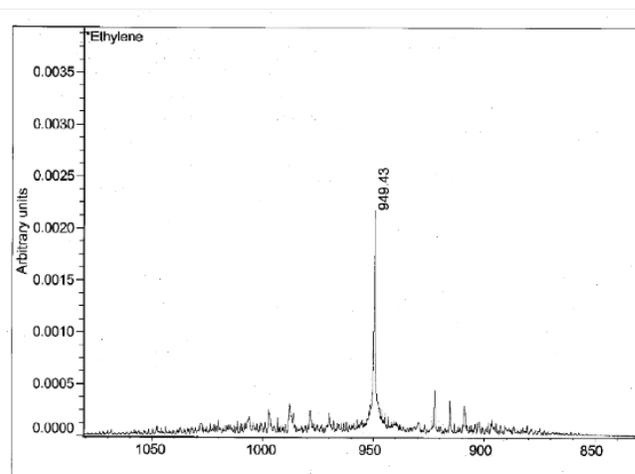
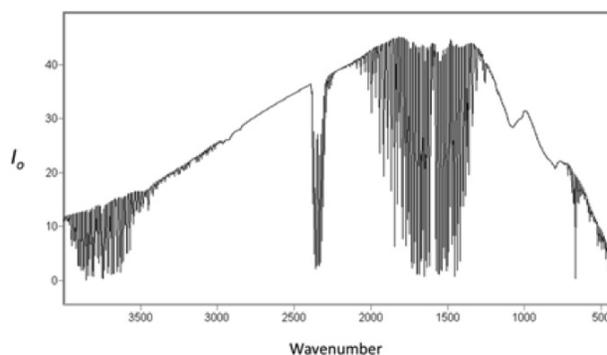


Figure 2. Uncorrected Background top showing strong bands from water, carbon dioxide, and from methane (top) and spectrum of 100 ppb of ethene taken with a 22 m long path cell (below). Ethene has a very sharp band that allows it to be readily determined in that region of the spectrum.

One option that should be considered is the use of long-path infrared spectroscopy that has been developed for monitoring trace gases and has been applied in the past by the DOD and EPA. Using a moderately high resolution of a half-wavenumber (0.5 cm⁻¹), the spectral determinations of many gases including ethene, methane, carbon dioxide, carbon monoxide, ozone, PAN, formaldehyde, and other key gases can be achieved at ppb or sub ppb levels using a telescope and reflector system that are now commercially available with a 500 m path length. Setting up these systems at colleges and universities around the region would not only allow for a data base to be obtained for long term trend analysis and evaluation of what is happening in our regions for key greenhouse and air pollutant gases as we begin to implement control strategies, but would also allow training of students in analytical spectroscopy.

Wouldn't it be a great thing if we were more proactive instead of reactive when dealing with the potential issues and problems from climate change in the future by recognizing it is a complex problem that will require us to start to gather better data now to allow us to address if a problem exists and if our solutions are actually working. Food for thought!

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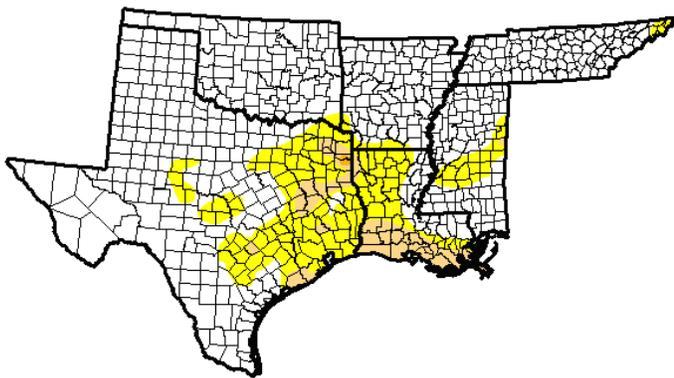
Drought Update

Luigi Romolo,
Southern Regional Climate Center

Drier than expected conditions across eastern Texas and Louisiana has led to the introduction of moderate drought. Much of this drought is located in the southern counties of Louisiana, and in north eastern Texas.

In Texas, agricultural effects were incredibly varied. Wineries were negatively impacted from the previous month's excessive rainfall as the grapes began growing fungi. The increase in rain early on in the month caused grasshoppers to migrate to the Panhandle area where there was less rain, reducing pesticide use in other regions. Chigger populations meanwhile benefited from the excess rainfall. The beginning of the month

brought hardships to the shellfish industry. The dry spell towards the end of the month meant the farmers were also able to better use their equipment without having to worry about them sticking in the mud. Cattle and most crops thrived during July. Excessive rainfall caused damage to several Texas State Parks in July. Overall, there were an estimated \$2.3 million dollars in damage, and over a dozen parks were closed. High winds postponed the first day of balloon races in East Texas. The triple digit heat was welcomed by a group of engineers in north Texas, who built solar powered cars that were judged by how long they could run. Some heavy rain also occurred late in the month for West Texas and caused flooding in El Paso and Amarillo (Information provided by the Texas Office of State Climatology).



Released Thursday, Aug 6, 2015
Mark Svoboda National Drought Mitigation Center

Drought Conditions (Percent Area)

	None	D0-D4	D1-D4	D2-D4	D3-D4	D4
Current	76.66	23.34	5.43	0.09	0.00	0.00
Last Week 7/28/2015	87.23	12.77	0.34	0.00	0.00	0.00
3 Months Ago 5/5/2015	69.59	30.41	22.78	13.98	5.16	1.48
Start of Calendar Year 12/31/2014	41.57	58.43	33.88	18.43	8.80	2.36
Start of Water Year 9/30/2014	41.74	58.26	35.49	22.66	8.47	1.98
One Year Ago 8/5/2014	44.85	55.15	38.73	24.34	9.13	1.79



Intensity:

- D0 Abnormally Dry
- D1 Moderate Drought
- D2 Severe Drought
- D3 Extreme Drought
- D4 Exceptional Drought

Above: Drought conditions in the Southern Region. Map is valid for August 4, 2015. Image is courtesy of National Drought Mitigation Center.

The Drought Monitor focuses on broad-scale conditions. Local conditions may vary. See accompanying text summary for forecast statements.

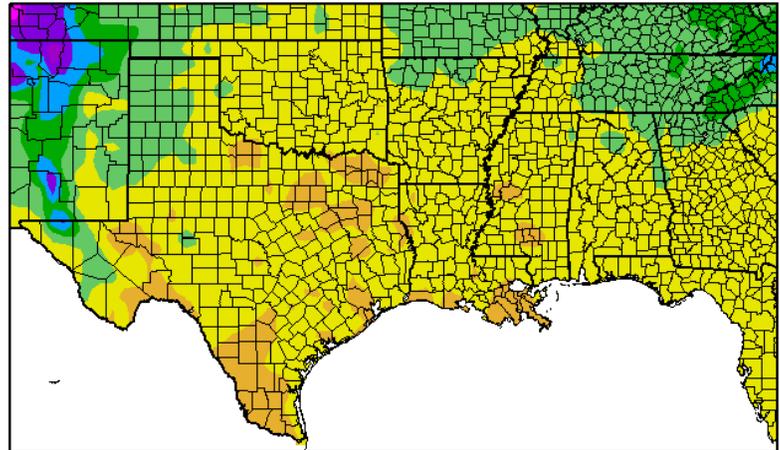
Southern Climate Monitor

Temperature Summary

Luigi Romolo,
Southern Regional Climate Center

July was a warmer than normal month across the entire southern region with almost all stations reporting average temperatures of at least 0-2 degrees F (0.00-1.11 degrees C) above normal. Temperature anomalies were slightly higher in the central portions of the region where many stations averaged between 2-4 degrees F (1.11-2.22 degrees C) above normal. This was also the case for counties within the Texas Trans Pecos Climate Division. The state-wide average temperatures for the month are as follows: Arkansas averaged 81.90 degrees F (27.72 degrees C), Louisiana averaged 84.30 degrees F (29.06 degrees C), Mississippi averaged 82.70 degrees F (28.17 degrees C), Oklahoma averaged 82.00 degrees F (27.78 degrees C), Tennessee averaged 78.30 degrees F (25.72 degrees C), and Texas averaged 83.10 degrees F (28.39 degrees C). For Louisiana, it was the third warmest July on record, and Mississippi experienced its eleventh warmest. Arkansas and Tennessee recorded their twenty-fourth and thirty-first warmest July on record, respectively. All other state ranking fell within the two middle quartiles and all records are based on data for the period 1895-2015.

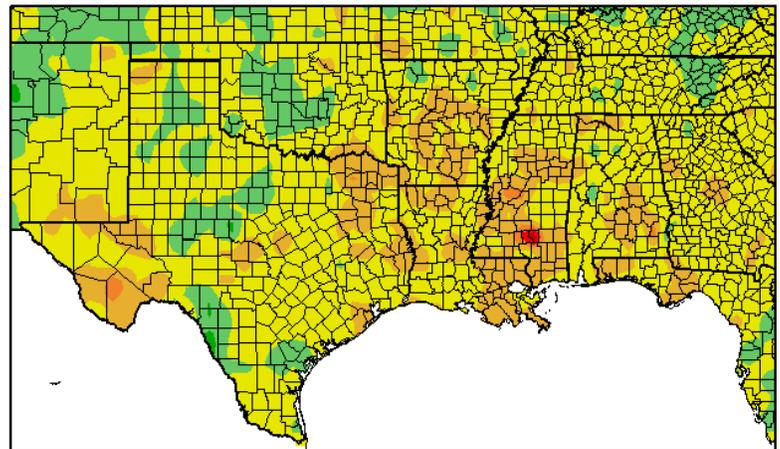
Temperature (F)
7/1/2015 - 7/31/2015



Generated 8/5/2015 at HPRCC using provisional data. Regional Climate Centers

Average July 2015 Temperature across the South

Departure from Normal Temperature (F)
7/1/2015 - 7/31/2015



Generated 8/5/2015 at HPRCC using provisional data. Regional Climate Centers

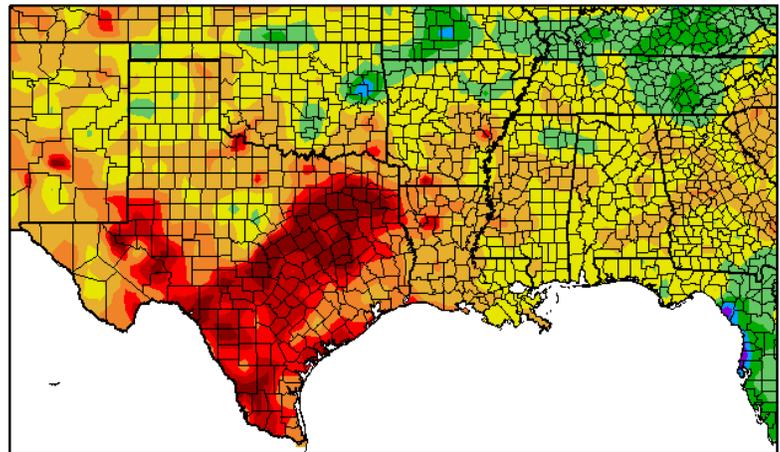
Average Temperature Departures from 1971-2000 for July 2015 across the South

Precipitation Summary

Luigi Romolo,
Southern Regional Climate Center

July precipitation in the Southern Region varied spatially from north to south, with northern counties experiencing a very wet month and southern counties experiencing a much drier than normal month. Counties extending from western Texas and Oklahoma through northern Arkansas averaged between one and a half to two times of normal precipitation. Conditions were quite the opposite in Louisiana and eastern/southern Texas, where a majority of stations averaged between five and fifty percent of normal, with many stations not seeing a drop of rain all month. The state-wide average precipitation totals for the month are as follows with: Arkansas reporting 5.08 inches (129.03 mm), Louisiana reporting 2.79 inches (70.87 mm), Mississippi reporting 4.51 inches (114.55 mm), Oklahoma reporting 5.10 inches (129.54 mm), Tennessee reporting 6.17 inches (156.72 mm), and Texas reporting 1.90 inches (48.26 mm). For Louisiana it was the ninth driest July on record, while Oklahoma experienced its thirteenth driest July. Conversely, Arkansas recorded their twenty-fourth wettest July on record, and for Oklahoma and Tennessee it was their thirteenth and seventeenth wettest, respectively. All other state rankings fell within the two middle quartiles and all records are based on data for the period 1895-2015.

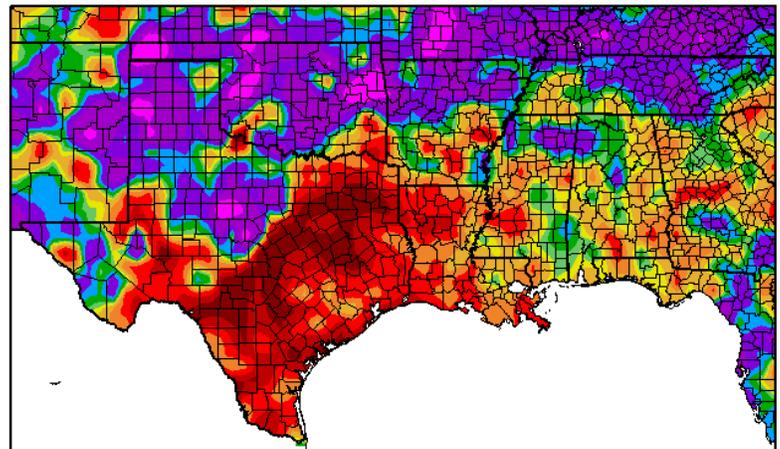
Precipitation (in)
7/1/2015 - 7/31/2015



Generated 8/5/2015 at HPRCC using provisional data. Regional Climate Centers

July 2015 Total Precipitation across the South

Percent of Normal Precipitation (%)
7/1/2015 - 7/31/2015

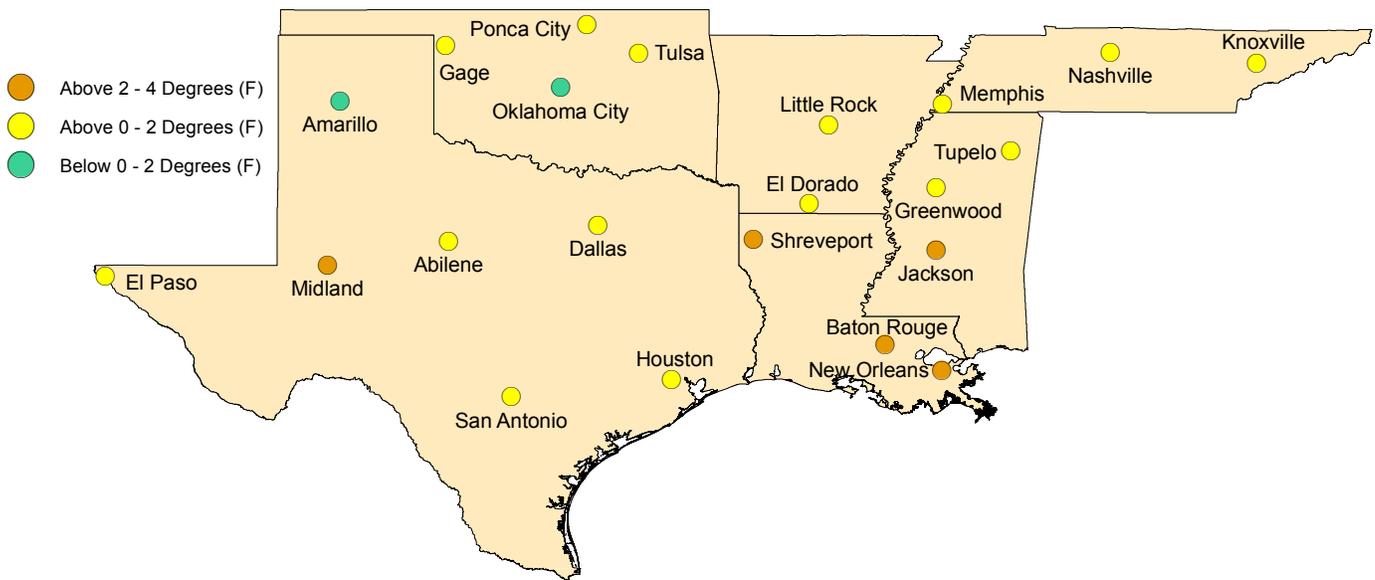


Generated 8/5/2015 at HPRCC using provisional data. Regional Climate Centers

Percent of 1971-2000 normal precipitation totals for July 2015 across the South

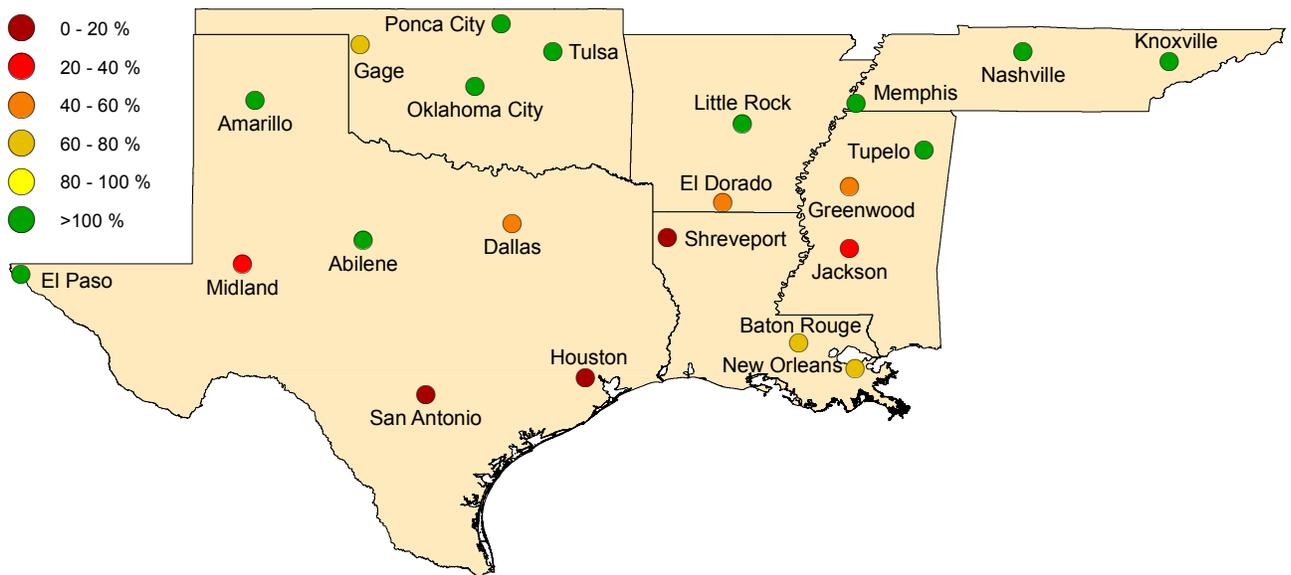
Regional Climate Perspective in Pictures

July Temperature Departure from Normal



July 2015 Temperature Departure from Normal from 1971-2000 for SCIPP Regional Cities

July Percent of Normal Precipitation



July 2015 Percent of 1971-2000 Normal Precipitation Totals for SCIPP Regional Cities

Climate Perspective

State	Temperature	Rank (1895-2011)	Precipitation	Rank (1895-2011)
Arkansas	81.90	24th Warmest	5.08	24th Wettest
Louisiana	84.30	3rd Warmest	2.79	9th Driest
Mississippi	82.70	11th Warmest	4.51	55th Driest
Oklahoma	82.00	50th Warmest	5.10	13th Wettest
Tennessee	78.30	31st Warmest	6.17	17th Wettest
Texas	83.10	35th Warmest	1.90	42nd Driest

State temperature and precipitation values and rankings for July 2015. Ranks are based on the National Climatic Data Center's Statewide, Regional, and National Dataset over the period 1895-2011.

Station Summaries Across the South

Station Summaries Across the South											
Station Name	Temperatures								Precipitation (inches)		
	Averages				Extremes				Totals		
	Max	Min	Mean	Depart	High	Date	Low	Date	Obs	Depart	%Norm
El Dorado, AR	93.7	73.3	83.5	1.8	100	07/29	67	07/31	2.01	-1.55	56
Little Rock, AR	93.9	75.4	84.6	1.8	101	07/29	69	07/06	4.76	1.49	146
Baton Rouge, LA	95.3	75.3	85.3	2.3	100	07/30	69	07/05	3.73	-1.23	75
New Orleans, LA	94.0	77.1	85.6	2.3	99	07/29	72	07/05	4.17	-1.76	70
Shreveport, LA	96.1	76.2	86.2	3.1	104	07/30	70	07/04	0.59	-3.06	16
Greenwood, MS	93.1	72.9	83.0	1.7	99	07/20	65	07/31	2.08	-1.52	58
Jackson, MS	95.0	74.4	84.7	3.1	101	07/30+	67	07/06	1.49	-3.32	31
Tupelo, MS	92.1	73.8	83.0	1.6	98	07/28	66	07/31	10.28	6.38	264
Gage, OK	94.1	69.2	81.7	1.4	105	07/13	59	07/08+	1.51	-0.39	79
Oklahoma City, OK	91.9	71.3	81.6	-1.4	98	07/20	64	07/08	7.31	4.38	249
Ponca City, OK	92.6	73.5	83.0	1.4	100	07/01	64	07/08+	6.01	2.68	180
Tulsa, OK	93.1	75.3	84.2	1.3	99	07/24	67	07/08+	6.72	3.36	200
Knoxville, TN	86.8	70.1	78.5	0.1	92	07/29+	66	07/16	6.49	1.41	128
Memphis, TN	92.7	76.4	84.5	1.9	99	07/29+	69	07/05	5.17	0.58	113
Nashville, TN	90.1	71.5	80.8	1.4	96	07/28	65	07/31	7.07	3.43	194
Abilene, TX	94.9	73.6	84.3	1.2	102	07/31	67	07/08	8.30	6.43	444
Amarillo, TX	89.7	66.7	78.2	-0.1	98	07/12	56	07/08	6.59	3.75	232
El Paso, TX	96.3	72.6	84.5	1.7	101	07/25+	66	07/11	2.88	1.33	186
Dallas, TX	96.4	77.8	87.1	1.8	104	07/30	73	07/10	0.92	-1.24	43
Houston, TX	95.6	76.5	86.1	1.7	101	07/30	71	07/02+	0.61	-3.18	16
Midland, TX	96.8	72.6	84.7	2.6	103	07/27	68	07/14+	0.72	-1.10	40
San Antonio, TX	94.7	76.5	85.6	1.0	100	07/31	70	07/02	0.07	-2.67	3

Summary of temperature and precipitation information from around the region for July 2015. Data provided by the Applied Climate Information System. On this chart, "depart" is the average's departure from the normal average, and "% norm" is the percentage of rainfall received compared with normal amounts of rainfall. Plus signs in the dates column denote that the extremes were reached on multiple wdays. Blushaded boxes represent cooler than normal temperatures; redshaded boxes denote warmer than normal temperatures; tan shades represent drier than normal conditions; and green shades denote wetter than normal conditions.

NOAA Updates 2015 Hurricane Season Prediction

Barry Keim, Louisiana State Climatologist, Louisiana State University

A couple of weeks ago - on August 6 - NOAA updated their prediction for the 2015 hurricane season. Little has changed from predictions made back in late May, except that NOAA is even more certain that we'll have a relatively quiet season, with perhaps even fewer storms. This is good news as we are now moving right into the teeth of the season which runs from about mid-August until the first week of October. For this season, NOAA is now projecting anywhere from 6-10 named storms, and of these, 1-4 will likely be hurricanes, and of these, 0-1 are likely to become major (Category 3-5) hurricanes. This is a dialed-down version of their May 2015 forecast, which had 6-11 named storms, 3-6 hurricanes, and 0-2 major hurricanes. NOAA

is also now 90 percent confident that we'll have a season with below-normal activity, whereas they were 70 percent certain in May. The reason for the upped confidence is that conditions mostly played out as predicted. El Nino has strengthened, perhaps even moreso than originally predicted, which has created wind sheer over the hurricane breeding grounds. In addition, the sea surface temperatures in the hurricane breeding grounds are running a little below normal. This is a great combination for a relatively quiet season. But, as everyone keeps saying, all it takes is one to ruin your season. So, be happy, but be vigilant. If you have any questions, feel free to contact me at keim@lsu.edu.

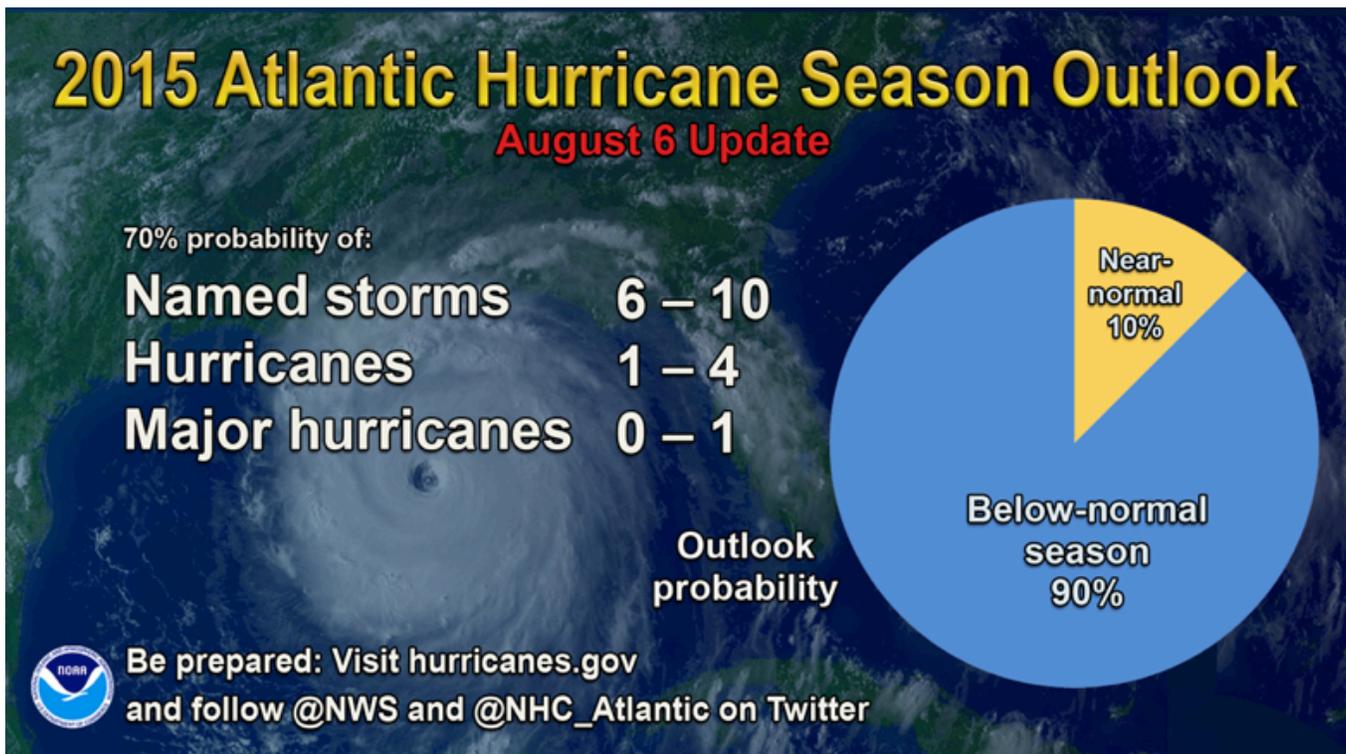


Figure 1. The National Oceanographic and Atmospheric Administration's August update for the the 2015 hurricane season. Graphic is available at http://www.noaanews.noaa.gov/stories2015/images/Outlook_2015_AUGUSTUPDATE_DRAFT3_1000.jpg.

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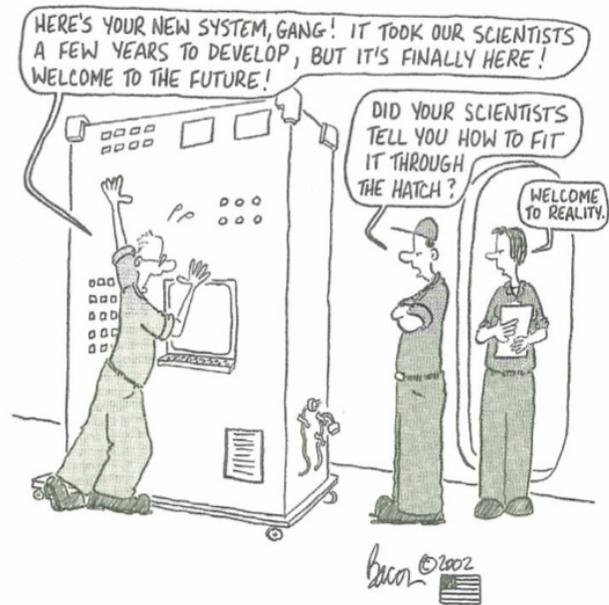
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For any questions pertaining to historical climate data across the states of Oklahoma, Texas, Arkansas, Louisiana, Mississippi, or Tennessee, please contact the Southern Regional Climate Center at [225-578-5021](tel:225-578-5021).

For questions or inquiries regarding research, experimental tool development, and engagement activities at the Southern Climate Impacts Planning Program, please contact us at [405-325-7809](tel:405-325-7809) or [225-578-8374](tel:225-578-8374).

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